Surfactant production and use in Germany: resource requirements and CO_2 emissions

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Abstract

Surfactants (surface-active agents) can be derived from both petrochemical feedstocks and renewable resources (e.g. oleochemicals). Renewable resources have the advantage that they contribute less to the greenhouse effect if harvested and grown sustainably. When comparing the contribution to the greenhouse effect, the life-cycle of the product should be analysed, covering the CO_2 emissions from production, use and degradation after disposal. In this paper, the use phase is only included for washing and cleaning agents since it is practically impossible to cover all the utilization processes for surfactants. At present, biomass-derived raw materials account for about one third of the material feedstocks for surfactant production in Germany. Within this partial life-cycle inventory, it was calculated that fossil CO_2 emissions of the commercially most important surfactants produced in Germany amounted to 1.5 Mt in 1996 (versus total chemical industry emissions of 125 Mt, including the equivalents of feedstock energy). Already today, the production of oleochemical feed-stocks avoids the emission of 0.35 Mt of fossil CO_2 p.a. (1996). Total substitution of oleochemical surfactants for petrochemical surfactants would enable a further reduction of 34%, reducing absolute emissions to 0.99 Mt. This is an overestimation of today's technical potential, but it might be attainable in the longer term. For surfactant applications in laundry detergents, lowering wash temperatures is also an interesting strategy to reduce CO_2 emissions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Surfactants; Material flow analysis; CO_2 emissions; Emission reduction; Life-cycle

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1. Introduction

Surfactants constitute an important group of chemical products, not only in terms of quantity, but also in view of the great variety of areas of application in households and commerce, in industry and agriculture. They are composed of a water-soluble ionic group, the hydrophilic portion, and a hydrocarbon chain, the hydrophobic portion, which together provide the compound with interfacial activity, as the nonabbreviated, nowadays less common term 'surface-active agent' indicates. In our daily life, we constantly come across surfactants, for instance, in detergents, cosmetics and food. In manufacturing processes, surfactants are used as antistatic agents, lubricants and levelling agents, e.g. for textile production, as flotation agents, e.g. in mining, oil production and wastewater treatment and as emulsifiers in the food industry and for the production of colorants, coatings and plastics. Fig. 1 gives an overview of the applications of surfactants in Germany.

Surfactants can be derived from both petrochemical feedstocks and renewable resources (plant and animal oils). They represent a particularly interesting product group since they were originally made from renewable resources whereas today, the majority is of petrochemical origin. Still, renewables have not lost their importance completely and processes for surfactant manufacture from both kinds of feedstocks are commonly used today. This leads to the question whether the use of renewables in surfactant production can contribute to savings of fossil resources, such as crude oil and natural gas, and to the reduction of fossil carbon dioxide emissions (CO_2) and hence, could be part of a strategy to mitigate the greenhouse gas effect. There is a good chance that the use of biomass could contribute to these goals because the carbon dioxide originating from biomass is equivalent to the amount which was previously withdrawn from the atmosphere during growth. However, in order to determine the net effect, the consumption of non-renewable energies for processing
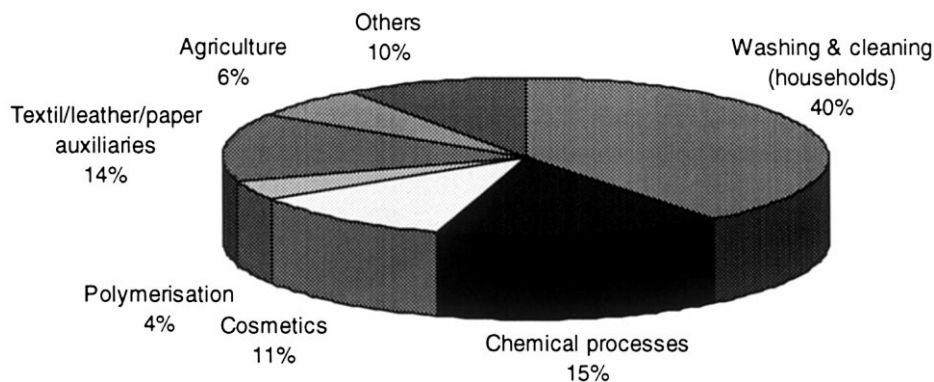

Fig. 1. Distribution of German surfactant production by fields of application in 1996 (Ungeheuer P. Personal communication, Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoffindustrie (TEGEWA), Frankfurt a. M. 1996/97). Note: only anionic and non-ionic detergents are covered which in total represent approximately 90% of the German surfactant market (without soap). Cationics, amphoterics and soaps are not included in this diagram.

the crops, the production of auxiliaries and materials required (e.g. fertilizers) and energy for transport all have to be taken into account.

It seems important to tackle these issues especially if one considers the current world-wide consumption of surfactants (9.3 Mt in 1995) and the expected growth rates in the near future, amounting to 3–4% per year on a global scale and 2–3% in Europe [1,2].

In this paper, we will focus on the situation in Germany. We will first analyse the current production structure and the associated material and energy requirements. In this context we will also investigate the quantities of the various intermediates used. In a second step, we will present a substitution strategy and its possible contribution to reducing CO_2 emissions.

This analysis is a part of an ongoing study dealing with the use of fossil fuels for the production of materials, the so-called non-energy use (e.g for plastics, lubricants, surfactants). The goals of this framework study are to make an inventory of the material flows, energy requirements and CO_2 emissions for Germany, including strategies for optimization, such as a shift of feedstocks towards biomass (this paper) or improvements in the fields of recycling and energy recovery [3,4].

2. Production structure

About thirty types of surfactant are produced in industrial quantities, but seven of these alone account for a major share of the German market, namely soaps, linear alkylbenzene sulphonate (LAS), secondary alkane sulphonate (SAS), alcohol sulphates (AS), alcohol ether sulphates (AES), alcohol ethoxylates (AE) and alkyl polyglucosides (APG). Fig. 2 gives an overview of the feedstock options for these surfactants. There are three categories of raw material requirements:
- minerals (sodium chloride, limestone, sulphur, oxygen, nitrogen),
- fossil resources (crude oil, natural gas, coal), and
- biomass-derived materials (vegetable oils, tallow, corn).

The most important vegetable oils used in surfactant production are palm oil, palm kernel oil and coconut oil. Palm oil (PO) is obtained from a pulp of the outer fleshy fruit of the tropical palm tree. Palm kernel oil (PKO) is extracted from the nut kernels of the same fruit cluster that yields palm oil. Coconut oil (CNO) is obtained by extraction from the dried fruit (copra) of the coconut palm tree [5].

As depicted in Fig. 2, LAS and SAS are exclusively based on fossil feedstocks. The type of raw material requirements for AS, AES and AE depends on the origin of the alkyl chains. These are either uniquely derived from fossil raw materials (crude oil and natural gas) or partly based on oleochemical feedstocks. The raw material inputs for APG are predominantly of oleochemical origin. For APG, small amounts of natural gas are used for methanol production. Palm oil based soap is the only surfactant which can be uniquely derived from vegetable oils, whereas small amounts of natural gas and coal are used to produce tallow-derived soap (not shown in Fig. 2). Apart from these raw material requirements, fossil fuels are required for transport and processing and to produce indirect material inputs, e.g. fertilizers and sulphur.
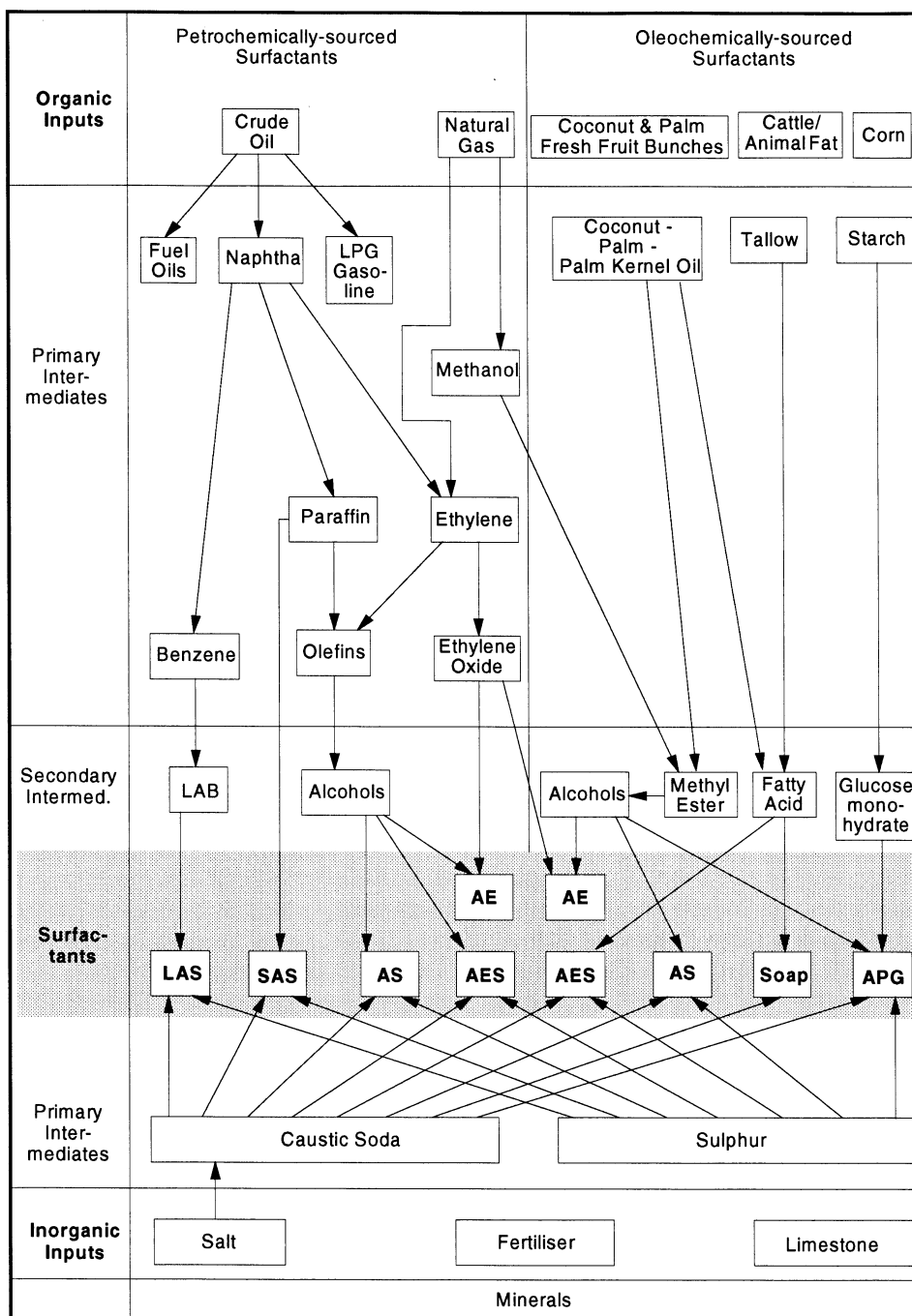
Fig. 2. Sourcing diagram for surfactants (following [6]). AE: Alcohol ethoxylates; AES: Alcohol ethoxy sulphates; APG: Alkyl polyglucosides; AS: Alcohol sulphates; LAS: Linear alkylbenzene sulphonates; LAB: Linear alkylbenzene; LPG: Liquefied petroleum gas; SAS: Secondary alkane sulphonate.

Table 1
Surfactant production in Germany in 1996 [7]

Type/compound	Production	
	kt	%
Anionics		
Soap	129	—
Linear alkylbenzene sulphonate (LAS-Pc[a])	100	—
Secondary alkane sulphonate (SAS-Pc)	40	—
AS	30	100
AS-Pc	18	60
AS-PKO	9	30
AS-CND	3	10
AS-PO	0	0
AES	80	100
AE$_3$S-Pc	24	30
AE$_3$S-PKO	16	20
AE$_3$S-CNO	40	50
Nonionics		
AE	165	100
AE$_3$-Pc	10	10[b]
AE$_3$-PKO	28	30
AE$_3$-CNO	10	10
AE$_7$-Pc	23	10
AE$_7$-PO	94	40
AE$_7$-CNO	0	0
AE$_{11}$-PO	0	0
APG[c]	20	100
APG-PKO	6	30
APG-CNO	14	70
Others[d]	305	—
Total production		
Without soap	740	
With soap	869	

Based on Ungeheuer P. (personal communication, Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoffindustrie (TEGEWA), Frankfurt a. M. 1996/97) and [7].
The products listed are manufactured from petrochemical and/or oleochemical raw materials. All oleochemical raw materials are produced abroad and imported to Germany. Surfactants are also traded, so the consumption differs from the production volumes listed.
[a] Pc, petrochemical feedstock.
[b] The percentages for AE$_3$ contain double countings, 60% are used for AE$_3$S production; the production figures in absolute terms have been corrected for double counting.
[c] Estimate based on personal communication with a surfactant producer.
[d] Including other anionic, nonionic, cationic and amphoteric surfactants.

Table 1 shows the production figures for surfactants in Germany. The data given cover the manufacture for use in all areas of application. Since surfactants are also traded—both as chemicals and as components of final products (e.g. washing powder)—the consumption figures for Germany differ from those given in Table 1.

It should also be noted that a part of the raw materials required to manufacture these surfactants are produced outside Germany and are imported.

A surfactant can be categorized according to the electrical charge in the chain-carrying portion of the molecule after dissociation in aqueous solution (Table 1): anionic (negative charge), cationic (positive charge), non-ionic (no charge) and amphoteric (containing both a positive and a negative group). Anionics are the commercially most important class, but they have recently lost some of their market share to non-ionics. Non-ionics represent the fastest growing type of surfactant due to their increased use in detergents, where they exhibit synergistic effects with other surfactants, and owing to their suitability for the manufacture of highly concentrated detergents or compact products. Cationics (mainly used for fabric softening and liquid household products) and amphoterics (e.g. used for bodycare preparations) have been restricted to comparatively small markets so far.

Soap belongs to the group of anionics. It is the oldest man-made surfactant and is still the leading surfactant on a global scale. However, in industrialized countries, soap has been replaced to a large extent by synthetic detergents due to its inferior washing properties. Soap also continues to face strong competition in the field of personal hygiene, which represents the largest remaining market.

3. Material flows

In the following, we will determine the amounts of intermediates required for the production of surfactants. We will exclude soap from further analysis since the production shares of the various soap blends are not available (Table 1). Moreover, soap cannot be considered a potential substitute for synthetic surfactants, due to its inferior properties and in consideration of market trends in the past. The group 'other surfactants' (Table 1) will not be followed up any further either, since there is no detailed information on the production volumes and processes of the individual types of compounds.

Having excluded these two groups, the types of surfactants to be analysed further are LAS, SAS, AS, AES, AE and APG. We will restrict ourselves to the main representatives among these types of surfactants, for which total production in Germany amounted to 435 kt in 1996 (Table 1, 740 kt–305 kt$_{Others}$). As can be derived from the composition formulas given in Table 1 half of this amount is currently produced from petrochemical feedstocks (215 kt), whereas the other half is either partly based on oleochemical materials or, in a minority of cases, made entirely from renewable resources. In order to be able to draw more precise conclusions, the amounts of resources required for the manufacture of the individual surfactants have to be determined.

Table 2 shows our results, which are based on the material requirements in specific terms published in the 'Life Cycle Inventory for Detergent Surfactant Production' (CEFIC/ECOSOL study) [8–13] and the production volumes presented in Table 1. Renewable primary intermediates account for about one third of the material feedstocks, with two thirds of the starting materials being of fossil origin.

Table 2
Consumption of primary intermediates for the production of selected surfactants in Germany in 1996

| | Petrochemical intermediates (kt) | | | | | | Biomass-derived intermediates (kt) | | | |
	Benzene	n-Paraffin	Ethylene for olefins	Ethylene for EO	Ethylene for alcohol	Methanol	Crude PKO	Crude CNO	Crude PO	Glucose mono-hydrate
LAS	25.1									
SAS-Pc		27.2								
AS-Pc		2.2	5.7							
AS-PKO						0.1	6.2			
AS-CNO						0.0		2.0		
AS-PO						0.0			0.0	
AE$_3$S-Pc		4.7	3.9	6.2	2.1	0.2				
AE$_3$S-PKO				4.4		0.4	7.9			
AE$_3$S-CNO				11.0				19.6		
AE$_3$-Pc		1.5	2.8	3.1	1.3	0.3				
AE$_3$-PKO				9.1		0.1	16.6			
AE$_3$-CNO				3.2				5.8		
AE$_7$-Pc		2.7	4.9	10.4	2.3	0.8				
AE$_7$-PO				45.0		0.0			38.8	
AE$_7$-CNO				0.0		0.0		0.0		
AE$_7$-PO				0.0		0.0			0.0	
APG-PKO							2.7			3.8
APG-CNO								6.2		8.8
Total	25.1	90.0	17.3	92.6	9.7	2.0	33.3	33.7	38.8	12.6
	←			236.8		→	←		118.4	→

Our own calculations based on Ungeheuer P (personal communication, Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoffindustrie (TEGEWA), Frankfurt a. M. 1996/97) and [7–13].

No data were available for AE$_7$-PO. It was therefore assumed that specific material inputs are equivalent to those of AE$_7$-PKO for which data are available. The surfactants listed are manufactured from petrochemical and/or oleochemical raw materials. All oleochemical raw materials are produced abroad and imported into Germany.

We can therefore conclude from our material flow analysis that there is great scope to increase the share of renewable resources in German surfactant production. In absolute terms, the manufacture of the selected surfactants in Germany consumes about 72000 t of palm/palm kernel oil and 34000 t of coconut oil annually (Table 2). This corresponds to nearly 75% of the total amount of palm/palm kernel and 30% of the coconut oil consumed for technical and industrial purposes in Germany. For petrochemical intermediates, we calculated that the respective shares are 35% for paraffins and 3% or less for the other materials.

The material requirements in specific terms which have been used to calculate the figures in Table 2 represent averages for the entire European production, so the specific values for Germany may differ. However, these differences can be assumed to be small due to the similar standard of process technology in industrialized countries.

4. Energy requirements and CO_2 emissions

In 1995, the European LCI Surfactant Study Group (CEFIC/ECOSOL) prepared life-cycle inventories (LCI) for the manufacture of surfactants [6,8–13], which have since been extended by impact assessments [14]. The system covered in these studies spans from the raw material extraction down to the factory gate. The CEFIC/ECOSOL study provides an excellent database which we will draw upon. Unlike our analysis, the CEFIC/ECOSOL study includes a whole range of different emissions; but they do not pursue the fate of surfactants after their production, nor do they provide aggregated results for Germany. Other studies do cover the last two aspects [15–18], but they do not distinguish between the types of surfactants and moreover, they limit their analysis to detergents.

The purpose of this paper is to investigate the CO_2 emissions caused by German surfactant production, covering both their manufacture and final disposal, and to compare the results with those of a substitution scenario. Our study represents a partial LCI since we do not include the energy requirements and emissions associated with the further processing of surfactants (e.g. the production of detergents), nor with the processes in which they are consumed. The only exception are surfactants used for detergent purposes (Section 5). Considering the wide range of surfactant use (Fig. 1) the inclusion of all the other fields of application would be an extremely extensive task. Moreover, energy consumption in the use phase is not determined—or only rarely determined—by the choice of the surfactant, but rather by consumer behaviour. Consequently, if the in-use phase were to be included, a constant amount would be added to all values, regardless of the type of surfactant. This would not change our findings concerning a shift towards oleo-chemical surfactants (Section 5). For the same reasons, the in-use phase was also excluded for most of the products analysed in our framework study [3].

On the other hand, the authors recognize that the purpose of this paper is limited in scope due to the evaluation of only CO_2 emissions and due to the exclusion of those phases within the product life which are considered to be insensitive to the

results. Undoubtedly, we would obtain more detailed results and a better understanding of the improvement options if more types of emissions were included in the comparison and if each phase of product life could be analysed in detail. However, we have to make compromises in view of the availability of information.

Before calculating CO_2 emissions, the energy requirements need to be investigated. Two types of energy are distinguished:

- fuels to power processes and for transportation, and
- fuels used as chemical feedstocks which elsewhere, are referred to as energy required as a material resource (EMR).

Table 3 shows our compilation of energy requirements in specific terms. Again, these data are based on the European average as published in the LCI surfactant study. In reality, the values may differ from country to country because of differences in production processes and modes of operation, but for reasons of confidentiality this information has not been disclosed. Maybe even more importantly, the differences in the fuel mix and efficiency of electricity generation among the various countries may cause some differences between the European average and values for one single country. Since the CEFIC/ECOSOL Study Group published their data in terms of primary energy (i.e. the consumption of electricity is not revealed), it was impossible to compile corrected data for Germany. However, we consider these differences to have only a marginal effect (sensitivity analyses which were performed in the CEFIC/ECOSOL Study to determine the effects of differing efficiencies and fuel mixes generally show small impacts on the results (see [6], p. 106)).

We introduced a correction to ensure a strict distinction between process energy and feedstocks. In the original data, process energy which is supplied by a part of the raw materials, e.g. the coconut shells used to fuel the tapahan, is included in the feedstock energy [19]. In Table 3, however, this energy was assigned to biomass-sourced process energy. With these corrections, the feedstock energy in Table 3 is defined as the amount of fuel which physically ends up in the final product. This will enable the accurate calculation of CO_2 emissions from surfactant degradation later on, i.e. the extension of system boundaries from cradle-to-factory gate to cradle-to-grave.

According to Table 3, the total energy requirements range from 51.9 GJ/t of surfactant (SAS-Pc) to 83.2 GJ/t (AE$_3$-Pc). LAS, SAS, oleochemical AS and APG-PKO are below average. Given the fact that the production technologies for LAS and SAS are already optimised to a large extent and involve fewer process steps compared with the other petrochemically-sourced surfactants, this is not surprising. Regarding the various compounds of the same type of surfactant (Table 3), it can be observed that the total energy demand is highest for compounds derived from petrochemicals, followed by compounds based on coconut oil.

It has to be recognised that greenhouse gas concentrations depend on the effective rather than the total emissions. Therefore, in this study, a distinction is made between fossil and non-fossil emissions. This assumes that there is no net increase in atmospheric CO_2 with emissions from biomass, harvested and grown sustainably, since this was only recently withdrawn from the atmosphere. In

Table 3
Specific energy requirements for surfactant production

GJ/t of product	Process energy[a,b]							Transport	Feedstock energy[b]				Energy		
	Gas	Oil	Coal	Biom.	Hydro	Nucl.	Total	Oil	Gas	Oil	Biom.	Total	Fossil	Biom.	Total[c]
LAS-Pc	8.52	6.80	4.60	0.00	0.43	2.29	22.64	1.30	0.00	36.90	0.00	36.90	58.1	0.0	60.9
SAS-Pc	8.06	1.94	4.96	0.00	0.24	3.59	18.79	0.96	0.00	32.20	0.00	32.20	48.1	0.0	51.9
AS-Pc	16.60	4.11	6.24	0.00	0.37	2.94	30.26	1.19	20.60	21.10	0.00	41.70	69.8	0.0	73.2
AS-PKO	7.10	6.54	5.05	6.15	0.88	1.95	27.67	1.68	0.35	0.00	26.15	26.50	20.7	32.2	55.8
AS-CNO	6.96	3.59	5.05	1.99	0.42	1.95	19.96	1.93	0.35	0.00	40.11	40.46	17.9	42.1	62.4
AS-PO	6.41	3.82	4.65	6.31	0.19	1.80	23.18	1.73	0.30	0.00	26.79	27.09	16.9	33.1	52.0
AE$_3$S-Pc	18.00	3.45	6.83	0.00	0.59	3.14	32.01	1.55	14.50	24.90	0.00	39.40	69.2	0.0	73.0
AE$_3$S-PKO	9.82	5.19	6.10	4.43	0.89	2.52	28.95	1.91	4.98	10.10	18.78	33.86	38.1	23.2	64.8
AE$_3$S-CNO	9.72	3.01	6.10	1.43	0.56	2.52	23.34	2.09	4.98	10.10	28.87	43.95	36.0	30.3	69.5
AE$_3$-Pc	18.80	3.55	4.93	0.00	0.33	2.80	30.41	1.35	24.20	27.30	0.00	51.50	80.1	0.0	83.2
AE$_3$-PKO	9.87	5.81	4.10	5.32	0.74	1.69	27.53	1.79	8.23	10.30	22.58	41.11	40.1	27.9	70.4
AE$_3$-CNO	9.67	3.19	4.10	1.71	0.35	1.69	20.71	2.01	8.23	10.30	34.79	53.32	37.5	36.5	76.1
AE$_7$-Pc	16.90	2.68	4.82	0.00	0.34	2.86	27.60	1.32	22.90	27.00	0.00	49.90	75.6	0.0	78.9
AE$_7$-PKO	10.50	4.39	4.20	3.72	0.62	2.09	25.52	1.71	12.00	15.10	15.78	42.88	47.9	19.5	70.1
AE$_7$-CNO	10.40	2.64	4.20	1.19	0.34	2.09	20.86	1.86	12.00	15.10	24.31	51.41	46.2	25.5	74.1
AE$_{11}$-PO	10.00	2.98	4.10	5.75	0.23	2.22	25.28	2.22	13.10	16.80	24.45	54.35	49.2	30.2	81.8
APG-PKO	12.20	6.60	6.51	4.03	0.60	1.69	31.63	1.99	0.00	0.00	27.07	27.07	27.3	31.1	60.7
APG-CNO	12.20	4.67	6.51	1.29	0.30	1.69	26.66	2.15	0.00	0.00	36.31	36.31	25.5	37.6	65.1

Process energy, transport and total energy data taken/calculated from [6]. Feedstock data for petrochemical surfactants from [6], for oleochemical surfactants from [9,10,12] and [13], respectively. Biomass feedstock data have been corrected for the share which is used to fuel the process (see text).
[a] Other energy sources, such as solar or wind energy, are used in negligibly small proportion and are thus not listed here.
[b] Feedstock for fertilizer production assigned to process energy.
[c] Including hydro, nuclear and other (solar, wind, etc.) energy sources.

contrast, CO_2 released from fossil materials contributes to the increase in concentration in the atmosphere. This does not mean that the production of biomass-derived products does not contribute at all to the intensified greenhouse effect, because external energy is needed for their production which in general, causes fossil CO_2 emissions. Hence, it is necessary to follow all the phases of the life-cycle which are sensitive to the final result before coming to a conclusion concerning the advantages of biomass-derived products in view of the CO_2 greenhouse gas effect. Thus, we will consider CO_2 emissions (fossil and non-fossil) resulting from both the production of surfactants—where, apart from fuel combustion, carbon is, for example, emitted via wastewater—and ultimately from their biological degradation.

Table 4 shows the CO_2 emissions calculated by combining the energy data in Table 3 with CO_2 emission factors. We used the following CO_2 emission factors (kg CO_2/GJ): natural gas 56, crude oil 74, coal 90, palm kernel oil 78, palm oil 78, coconut oil 92, corn 85. The data give the CO_2 equivalents of the carbon which these resources contain. This is identical with the amount of CO_2 set free during combustion (data sources for fossil resources: [23], figure for coal is an own estimate based on individual values for all countries covered in the ECOSOL study. Data sources for biomass resources: [9], own calculations; figure for corn is an own estimate). The data presented in Table 4 are displayed as a bar diagram in Fig. 3. CO_2 emissions from combustion are referred to as 'fuel-related' and all the other emissions are summarized as 'feedstock-related'. Total fossil CO_2 emissions range from 1180 (AS-PO) to 5210 kg/t of product (AE_3-Pc). Surfactants made from coconut oil (CNO) show high total emissions (covering fossil and non-fossil CO_2) which is due to the high CO_2 emission factor of coconut oil (92 kg CO_2/GJ);
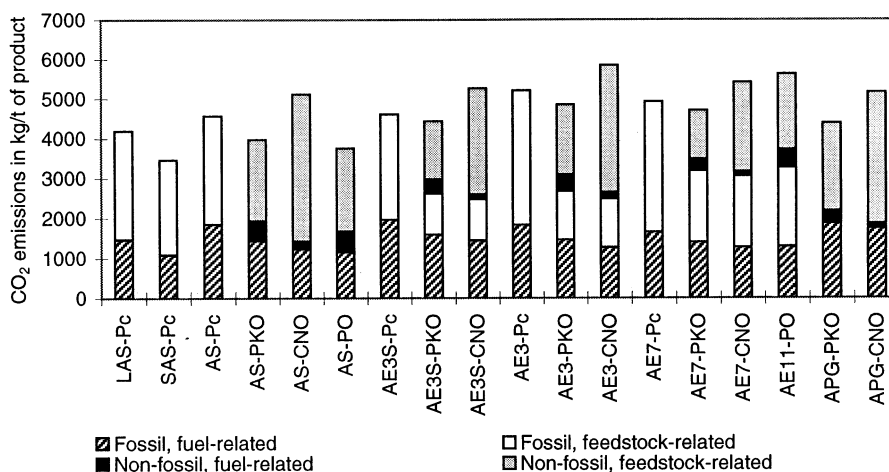

Fig. 3. CO_2 emissions for surfactants (based on own calculations, see text).

Table 4
CO_2 emissions for surfactants (based on own calculations, see text)

| | Specific CO_2 emissions in kg/t of product | | | | | | Total |
| | Fossil | | | Non-fossil | | | |
	Fuel-related	Feedstock-related	Total	Fuel-related	Feedstock-related	Total[a]	
LAS-Pc	1470	2730	4200	0	0	0	4200
SAS-Pc	1090	2380	3470	0	0	0	3470
AS-Pc	1850	2720	4570	0	0	0	4570
AS-PKO	1440	20	1450	480	2040	2520	3970
AS-CND	1230	20	1250	180	3690	3870	5120
AS-PO	1160	20	1180	490	2090	2580	3760
AE_3S-Pc	1960	2650	4610	0	0	0	4610
AE_3S-PKO	1590	1030	2620	350	1460	1810	4430
AE_3S-CNO	1440	1030	2470	130	2660	2790	5250
AE_3-Pc	1830	3380	5210	0	0	0	5210
AE_3-PKO	1460	1220	2690	410	1760	2180	4860
AE_3-CNO	1270	1220	2500	160	3200	3360	5860
AE_7-Pc	1650	3280	4930	0	0	0	4930
AE_7-PKO	1400	1790	3190	290	1230	1520	4710
AE_7-CNO	1270	1790	3060	110	2240	2350	5410
AE_{11}-PO	1290	1980	3270	450	1910	2360	5630
APG-PKO	1870	0	1870	310	2210[b]	2520	4390
APG-CNO	1740	0	1740	120	3300[b]	3420	5160

[a] Also referred to as net CO_2 emissions.
[b] Including CO_2 from limestone production.

however, fossil CO_2 from these compounds is considerably lower than from petrochemical surfactants. Fossil emissions higher than 4000 kg/t can be observed for all the petrochemical surfactants except for SAS with about 3500 kg/t. Oleochemical alcohol sulphates and alkyl polyglucosides show fossil CO_2 emissions below 2000 kg/t, i.e. they contribute less to the CO_2 greenhouse effect. The share of feedstock-related emissions (both fossil and non-fossil) ranges between 50 (APG-PKO) and 75% (AE_3-CNO) of total emissions, which indicates the importance of including the emissions occurring after surfactant production.

5. CO_2 emission reduction by surfactant substitution

There is a whole range of measures to reduce CO_2 emissions. Energy-related emissions can be curbed by improving the energy efficiency of production processes and energy supply systems, by switching to low carbon fossil fuels (e.g. natural gas) or to non-fossil energy sources which are either carbon-free (e.g. nuclear, wind) or carbon-neutral (biomass). An example for emission abatement in the use phase are detergents that function better at lower wash temperatures. Strategies aiming at feedstock-related emission reductions include an improvement of yields in production processes, recycling and re-use (usually not applicable to surfactants) and product substitution. In this section we will focus on the last option by analysing the reduction potential by substituting oleochemical surfactants for petrochemical surfactants.

Soap shows very low specific CO_2 emissions, but will not be considered as a substitute because, in most application areas, soap can no longer achieve the performance standards of the other anionic surfactants investigated.

It has to be emphasized that surfactants usually cannot be replaced simply on an equal mass basis (1 kg of surfactant A replacing 1 kg of surfactant B). The surfactants examined in this paper cover a variety of different structural and functional types with different properties and characteristics. In detergent preparations, as in many other applications, surfactants are only one component of rather complex systems. Typically, a special mixture of anionic and non-ionic surfactants in which the characteristics of each component are intended to supplement the others is carefully designed in order to deliver the desired performance under particular conditions. Consequently, it is generally not possible to replace one surfactant by another without making further adjustments, i.e. changing other components or altering the performance characteristics. Apart from technological feasibility, economic parameters, such as production costs and raw material prices, must also be taken into account. A shift in favour of oleochemical surfactants would require an expansion of the land area used to grow renewable resources, which possibly represents a further obstacle. On the other hand, legislative and political developments may support such a shift in the future.

We calculated a scenario where all the petrochemical AS, AES, and AE compounds are substituted by their CNO-based counterparts. LAS and SAS are replaced by AS-CNO and AES-CNO respectively. Fig. 4 depicts the comparison of
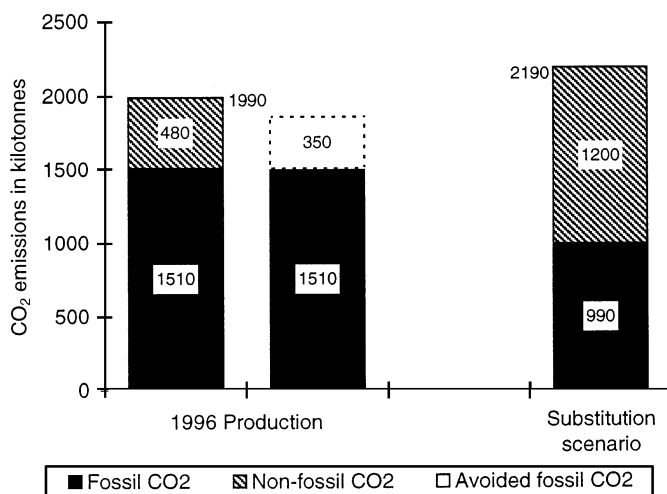
Fig. 4. CO_2 emissions caused by surfactant production in Germany (1996 basis).

this scenario with the current production structure (1996). (No data were available for AE_7-PO. It was therefore assumed that specific CO_2 emissions are identical with those of AE_7-PKO for which data are available.) Total emissions including those from fossil and non-fossil sources increase from 1.99 to 2.19 Mt CO_2 which is due to the high CO_2 emission factor of coconut oil. What is more relevant from the greenhouse gas point of view is the fact that total fossil CO_2 emissions (net CO_2) decrease from 1.51 to 0.99 Mt, i.e. by 34%. Already in 1996, approximately 0.35 Mt of fossil CO_2 emissions were avoided by the production of oleochemical surfactants. This figure was determined by calculating the effect of replacing all oleochemical surfactants by petrochemical products for which the weighted average of fossil CO_2 emissions amounted to 4270 kg/t in 1996 (total of fuel-related and feedstock-related CO_2).

Our scenario describing the substitution of petrochemical surfactants by CNO compounds overestimates the available emission reduction potential according to the current state-of-the-art, since the complete replacement of petrochemical surfactants would require additional R&D work and may not be feasible for all products. Oleochemical and petrochemical raw materials show divergent ranges of chain-lengths which lead to differences in product properties. In some cases, these differences can be compensated by minor or moderate changes in formulation. Exceptions excluded, this is the situation in the case of LAS, SAS and AES, which constitute about three quarters of the total petrochemical surfactant production in Germany (Table 1). Here, the economics represent the main obstacle to a change of feedstocks. In other cases however, the replacement of petrochemical surfactants by oleochemical products does not seem to be viable on the basis of today's knowledge.

On the other hand, our assumption of total substitution only refers to the six types of surfactants studied in this paper, so further opportunities may be available in the group of 'other surfactants'.

6. Discussion and conclusions

We can conclude from the last section that the assumption of total substitution of petrochemical surfactants is an overestimation of today's technical potential and this also applies to our calculations of the potential for mitigating CO_2 emissions for the six types of surfactants analysed. However, if longer time spans are allowed for adaptation and the scope of analysis is expanded to include the entire production of surfactants, this overestimation may be reduced or even eliminated. This leads to the conclusion that the calculated reduction by 34% might be attainable in the longer term.

It has to be emphasized that this figure does not include the effects of substitutions among the subgroups of surfactants (e.g. replacement of AE by APG; exceptions: LAS and SAS). More importantly, it does not include carbon abatement options for energy-related emissions in production and in the use phase, the reason being the scope of the framework study [3]. However, it can be estimated on the basis of other studies [16–18,20] that on average, the CO_2 emissions from the washing process represent about 60 to 80% of a surfactant's total CO_2 emissions throughout the life-cycle (including the use phase) and that lowering wash temperatures in Germany could save about 40% of the emissions which are released in the use phase. Consequently, energy savings in the use phase could decrease CO_2 emissions throughout the life-cycle by about 25 to 30%, which outweighs the saving potential due to the complete substitution of petrochemical surfactants by about a factor of two to four. This is a first indication that savings in the washing cycle are more promising than material substitution. However, these figures only apply to the use of surfactants in detergents which represent approximately 40% fo the surfactant market (Fig. 1). Further analyses are required to determine whether there is a comparable saving potential in the use phase for non-detergent applications of surfactants (Fig. 1) and to obtain a better understanding of the parameter ranges (e.g. by distinguishing between regular and compact detergents) and uncertainties. The challenge of climate change is to achieve substantial reductions in greenhouse gas emissions. Hence, CO_2 reduction by changing the feedstock may still become attractive. Material substitution also gains relative importance the lower the contribution of the use phase becomes, which may be a trend in the next few years.

Based on discussions with experts in the field, we chose 1 t of surfactant as the basis of our comparison (functional unit). This may be a shortcoming of this analysis. The reason is that—depending on the type of surfactant—different amounts might be required to provide the same service. This may also hinge on the field of application under consideration and on the composition of other components in the blend (e.g. enzymes). However, no information on replacement factors was available for this study.

It must also be borne in mind that our analysis excludes important greenhouse gases, such as CH_4 and N_2O, and that other environmental impacts were not taken into account.[1] Again, this is partly a result of the project context, and partly due to the lack of data, especially for degradation and the in-use phase. An improved analysis would have to overcome these shortcomings. It should also reflect the German situation regarding the process technologies applied and the specific emissions of the national electricity generation.

The quality of the data has a direct impact on the reliability of our results. Therefore it is worth pointing out that the variability of the data published in the CEFIC/ECOSOL study is reported to lie in the range of 10% for energy and 25% for emissions (with 95% confidence). Since we derived our figures for CO_2 emissions from energy data (process energy and feedstock energy) the uncertainty of our analysis should be around $\pm 10\%$. On the other hand, we should mention that neither these uncertainty ranges nor the individual CEFIC/ECOSOL data for the various surfactant systems are verifiable. Conducting a peer review—as in the CEFIC/ECOSOL study—definitely helps to avoid data inconsistencies, but it cannot be a guarantee considering the complexity of flows and the possible differences in understanding and reporting methods as described by Ayres [21]. These are further reasons to treat the results of this paper with some caution.

To put our results into perspective, we can draw a comparison with the chemical sector. In total, the chemical industry emits about 48.4 Mt of fuel-related fossil CO_2 (equivalents from electricity consumption included) [22] and the delayed, fossil CO_2 emissions from feedstock energy (non-energy use) are estimated at 77 Mt [3], adding up to approximately 125 Mt (1996). Fossil CO_2 emissions from the surfactants included in this partial LCI (1.51 t) represent only 1.2% of this total. But product substitution alone could curb these emissions by a maximum of 34%, which is equivalent to a respectable percentage of 0.4% of the total CO_2 emissions currently released by the chemical industry. The emergence of new surfactants on the market, such as alkyl polyglucosides (APO) and glucose amides (GA) might indicate that there is already a trend towards the increased use of renewable resources in surfactant production. On the other hand, these figures show that a complete shift towards oleochemical surfactants would lead to relatively small reductions com-

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[1] For CH_4, the ECOSOL study provides emission data for the system cradle-to-factory gate. We can use these data for a first estimation since it can be assumed that CH_4 emissions from degradation rather depend on the ambient conditions than on the type of surfactant. If we weigh CH_4 emissions with the GWP factor of 21 (100 years time horizon) this increases our earlier results by slightly less than 2% both for the current situation (1996) and the substitution scenario. The increase is so small even in the substitution scenario since we there assumed the replacement of petrochemical surfactants by CNO-based products. These, however, show negligible cradle-to-factory gate CH_4 emissions according to the ECOSOL study. PO- and PKO-based surfactants, on the other hand, do show considerable CH_4 emissions, which could be reduced to a large extent by collecting and using the biogas emitted from the so-called ponding systems, the purpose of which is to treat the palm oil mill effluent. Hence, this improvement measure should be implemented before increasing the shares of PO- and PKO-surfactants within a GHG minimization strategy. The question whether the inclusion of N_2O would change the findings cannot be answered since no data are available.

pared to the total emissions of industry and even more so, if the entire economy is taken as a reference (ca. 900 Mt CO_2 p.a.). The reason is that the surfactants analysed in this paper account for only about 2% of the total manufacture of organic chemicals and petrochemical products in Germany [3].

Ecological aspects will continue to play an important role in the future. If the general sensitivity to climate change increases, surfactant producers may encounter an additional stimulus to alter their portfolio product range in favour of products made from natural resources. In this case, cradle-to-grave LCIs and impact assessments for surfactants will have to be conducted in order to provide a sound foundation for decision-makers. The authors recognize that their own work is limited in scope due to the evaluation of CO_2 emissions only and due to the exclusion of the formulation step and the use phase. Especially, energy saving potentials due to consumer habits in detergent use may be more easily accessible and more economic than material substitution, and there might be even more effective, low-cost measures to reduce emissions, e.g. by improving the energy supply system. Moreover, other emissions and also the energy requirements for non-organic materials have to be considered prior to coming to final recommendations. On the other hand, limited resources have so far restricted the application of full-size LCAs to a relatively small number of products (e.g. washing powder), whereas we have chosen a simplified methodology with the advantage of being able to cover the entire production of surfactants.

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